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(54) Title: FABRIC CONDITIONERS (57) Abstract <p>This invention relates to fabric conditioning formulations containing as thickeners a cross-linked cationic polymer of an ethylenically unsaturated monomer or blend of monomers, wherein the cross-linking agent is 5-45 ppm of a cross-linking agent comprising polyethylenic functions. An example of such a cross-linking agent is methylene bisacrylamide. Such thickeners do not contribute to the opacity of the formulations and have a relatively good viscosity stability.</p>		

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FABRIC CONDITIONERS

This invention relates to fabric conditioning formulations. Most domestic detergents use the thickening properties of the surfactant ingredients and/or added salts to achieve the rheology desired for a particular application, preferably to avoid extra costs. However in many cases either the formulation is not stable physically or rheologically, or the rheology cannot be adjusted to that required, or, the ingredients have no rheology modifying properties over the useful range of combinations. In this case, the common practice is to use polymeric or mineral thickeners with suitable properties to build the rheological properties of the product. The most cost effective thickeners are usually chosen bearing in mind the limitations of formulating the thickener into the formulation. One particular aspect of thickening domestic detergent products is to improve product appeal to consumers. Another aspect closely related to improving product appearance is to adjust the appearance of the product by adding opacifiers.

Rinse-cycle fabric conditioners are mainly based on fatty cationic surfactants, used either alone or in combination with suitable non-ionic/fatty co-softeners, which are attracted to a fabric surface where they adsorb and impart a soft handle or feel. Minor ingredients may be added which improve stability, in addition to conventional colouring agents and perfumes. In other types of formulation, the main role of the cationic component is to render the other neutral fatty softeners as surface substantive, so they too are carried to the fabric surface to create a soft handle or

feel. It is known that products with viscosities between about 100-400cP at 20sec-1(25°C) are consistently preferred to products with around half the respective viscosity or less at a shear rate consistent with consumers pouring the product or observing the product flowing on inclined surfaces.

It is well known that controlling the rheology and physical stability of cationic softener formulations is difficult. This is due to the fact that cationic surfactants are disrupted and rendered ineffective by a wide range of materials. Anionic species, either dissolved or suspended may adsorb or precipitate the surfactant, causing both rheological and physical instability i.e. the product may become too thick or too thin, or phase separation of the aqueous phase may occur. Thus, unless used to form neutral fatty softening species or to deliberately thin the formulation e.g. liquid concentrates, anionic surfactants and additives are avoided by the industry. The formulations cannot therefore be thickened using anionic polymer thickeners. Mineral thickeners with exchangeable cations e.g. montmorillonite clays, usually cause instability, or do so when the surfaces become charged or polarised in aqueous dispersion.

Neutral and cationic polymers would be expected to be more stable in the presence of fatty cationic softeners. Such polymers are commercially available and, in the case of substantially water-based products in which they are soluble or dispersible, the polymers are substantially linear in structure. Such polymers are effective because they are essentially completely dissolved in the aqueous phase, where they may either structure the aqueous phase or physically interact with either other polymers and/or the surfactant phase. These polymers suffer from one or more of the following disadvantages:

- 1) The dissolved polymer is free to interact at the molecular level with the dispersed cationic softener, and may flocculate or precipitate the softener and co-softeners. "Dissolved" in this context means that the polymer at user concentration forms clear or slightly hazy solutions.

- 2) Such soluble polymers are unlikely to contribute to the opacity of the formulation. Thus dilute fabric conditioners may require additional opacifiers. This is a significant added cost to the formulation.
- 5 3) Experience shows that soluble cationic polymers are less stable than nonionic/neutral polymers in the longer term, presumably because the dissolved polymer behaves partly as an electrolyte, thereby causing osmotic and electrostatic instability in the cationic disperse phase.
- 10 4) The rheological properties of these soluble polymers tend to be non-linear over the concentration range where perceivable thickening occurs. Beyond certain values e.g. 1% w/w concentration, the viscosity rises so rapidly that viscosity control may be a problem.
- 15 5) Where the dissolved polymer precipitates itself or flocculates the cationic surfactant, it is difficult to redisperse the polymer and regain the thickening effect.
- 6) Effectiveness of the thickening performance in these soluble polymers is retained by supplying as 100% active materials. These materials, unless expensively modified, can be difficult to disperse and may require expensive equipment to achieve dissolution.
- 20 7) Cationic and high molecular weight polymers would be expected to build up irreversibly on treated fabric.
- 8) Naturally derived polymers e.g. locust bean and guar gums, may be degraded by contaminant bacterial enzymes, causing loss of
- 25 viscosity in the product. Polymers derived from fermentation processes may also themselves be contaminated by bacteria with risk of product spoilage.
- 9) Many natural and synthetic polymers are unstable in the pH range e.g. 2.5-5 where rinse conditioners are normally formulated.
- 30 It has now been found that substantially all these problems can be mitigated by using a crosslinked, acrylamide copolymer containing cationic groups as thickener which also obviates the need for a separate opacifier.
- Accordingly, the present invention is an aqueous based fabric
- 35 conditioning formulation comprising a water dispersible cationic

softener and a thickener characterised in that the thickener is a cross-linked cationic polymer that is derivable from a water soluble cationic ethylenically unsaturated monomer or blend of monomers, which is cross-linked by 5 to 45ppm of a cross-linking agent comprising polyethylenic functions.

The cross-linked, cationic polymers, (hereafter "CP"), are formed from monoethylenically unsaturated monomer that is either a water soluble cationic monomer or is a cationic blend of monomers that may consist of cationic monomers alone or may consist of a mixture of cationic and non-ionic monomers in the presence of a cross-linking agent. If a blend of monomers is being used then part of the blend may have a low water solubility providing the blend is water soluble. The monomers can be allyl monomers but are generally vinyl, preferably acrylic.

Suitably, the cationic polymers are derivable from cationic monomers comprising one or more of (a) dialkylaminoalkyl-acrylates and methacrylates, especially dialkylaminoethyl acrylate, (b) dialkylaminoalkyl-acrylamides or -methacrylamides and (c) the quaternary or acid salts of (a) or (b), for instance methacrylamidopropyl trimethyl ammonium chloride and Mannich products such as quaternised dialkylaminomethylacrylamides. Alkyl groups are generally C₁₋₄ alkyl.

Suitable non-ionic monomers are acrylamide, methacrylamide, N-vinyl pyrrolidone, and lower alkyl water insoluble acrylic (or other ethylenically unsaturated) monomers such as methyl methacrylate, styrene or acrylonitrile which may be included in sufficiently small amounts so that the blend is soluble.

Blends of 5-90%, preferably 5-50%, acrylamide with dialkylaminoalkyl-acrylate or, preferably -methacrylate as acid addition or quaternary addition salts, or, cationic homopolymers (containing no acrylyamide groups) are preferred.

The monomers can contain hydrophobic groups, e.g., as described in KP-A-0172723, for instance on page 10 of that specification. If the monomer is to impart insolubility to the polymer, ethoxy chains, if any, should be short or absent, i.e., n=0. The allyl ether

monomers are especially preferred.

The cationic polymer must be added while in the form of particles below 10 micrometers in size, and preferably below 2 micrometers in size. These can be made by comminuting a cross-linked polymer gel but preferably the particles are formed initially in the cross-linked state. The particles may be added to the aqueous solution as disintegratable aggregates or pellets, but preferably are added as dispersion in a liquid, generally a non-aqueous liquid such as a hydrocarbon. This dispersion may be made by dispersing preformed particles in the liquid but is preferably made by reverse phase polymerisation of the monomer or monomer blend in the presence of the cross linker.

The monoethylenically unsaturated starting material may be contaminated with a small amount of crosslinking agent and the amount of additional cross-linking agent that is added will therefore be selected having regard to this. Preferably the monoethylenically unsaturated material is as free of cross-linking agent as is commercially possible, for instance containing cross-linking agent in an amount that gives cross-linking or chain branching less than is given by e.g. 1 ppm of a cross-linking agent comprising polyethylenic functions used in the present invention. By the term "polyethylenic functions" as used herein and throughout the specification is meant cross-linking agents which have two or more ethylenically unsaturated groups per molecule of the agent. Thus, an example of such an agent is methylene bisacrylamide (hereafter "MBA"). The amount of cross-linking agent with polyethylenic functions e.g. MBA that is added is at least 5 ppm and upto 45 ppm (based on monomer), generally from 10 to 40 ppm. The precise amount will depend upon the polymerisation and other processing conditions. Instead of using MBA, cross-linking may be by equally achieved by using effective amounts of other diethylenically unsaturated compounds such as ethylene glycol di-acrylate, diacrylamide, cyanomethylacrylate, vinyloxyethylacrylate or methacrylate and other means of cross linking, e.g., formaldehyde or glyoxal or metal salt addition.

Preferably a water-soluble cross-linking agent is used.

The degree of non-linearity can additionally be controlled by the inclusion of chain transfer agents in the polymerisation mixture. Their use, in combination with cross-linking agent, will tend to promote chain branching rather than cross linking. Amounts may vary widely. For instance 1,000 to 5,000 ppm (based on monomer) of a moderate chain transfer agent such as isopropyl alcohol may be suitable whilst much lower amounts, typically 100 to 500 ppm, of more effective chain branching agents such as mercaptoethanol are useful. Often, however, adequate results are obtained by conducting polymerisation under conventional conditions without deliberate addition of chain transfer agents, using commercially pure monoethylenically unsaturated monomer together with the specified amount of MBA or other cross-linking agent.

Preferred CP's are often formed from 0 to 40%w/w acrylamide and 100 to 60%w/w dialkylaminoethyl methacrylate quaternary salt (for instance 20% acrylamide 80% dimethylaminoethyl methacrylate quaternary salt) cross linked with 10 to 40 ppm, preferably 10-30 ppm of MBA or other cross linker. All parts and percentages are by weight. The precise optimum for any particular composition can be determined by observing the properties of the composition when thickened with the chosen amount of a range of CP's differing from one another solely by differing the amounts of MBA from 5 to 45 ppm.

The amount of CP typically may be in the range of 0.01% to 0.5%, often 0.02% to 0.2%, by weight CP based on the aqueous composition.

The polymerisation conditions are preferably such that the polymer has, if uncross-linked, a notional high molecular weight of 5 million to 30 million and an intrinsic viscosity (hereafter IV) of above 4, preferably above 6, e.g., up to 10 or 15 dl/g. If the polymer is cross linked (CP) it is preferably polymerised such that it would have such molecular weight if it had been made in the absence of cross linking agent. However cross linking will reduce the IV but the shearing may then cause the IV to increase, as

explained below.

The particle size in the emulsion or reverse phase polymerisation mixture may be controlled by the degree of shear applied to the monomers and by the possible presence of emulsifying agent. Emulsion polymerisation may be utilised when polymerising, for instance, water insoluble monomers such as acrylic esters or water insoluble but acid soluble monomers such as amines (the resultant CP being distributed into acidic aqueous composition) but generally reverse phase emulsion or suspension polymerisation is utilised when the monomer or monomer blend is soluble in water. The aqueous monomer is emulsified into a suitable non-aqueous liquid, generally in the presence of a water in oil emulsifier, generally in an amount below the critical micell concentration. Emulsifiers, stabilisers, non-aqueous liquids and other reverse phase polymerisation materials and process details are described in, for instance, EP-A-0126528. The CP particles may be dehydrated, for instance by subjecting the dispersion to azeotropic distillation.

The liquid product from the reverse phase polymerisation or emulsion polymerisation is generally used as such, without separation of the polymer particles from it, but if desired dried polymer particles may be separated from the dispersion in known manner. Because these dry particles will be very dusty they should preferably be formed into pellets that will disintegrate upon addition to water.

The polymer-in-oil emulsion that results from reverse phase polymerisation may be added to the composition to be thickened in the presence of oil-in-water emulsifier in conventional manner.

When the polymeric material is cross linked and cationic, and in particular when it is a copolymer of acrylamide with at least 5%, and preferably at least 10%, by weight dialkylamino alkyl acrylate (generally as acid addition or quaternary ammonium salt) the degree of non-linearity is preferably such that the CP has an ionic regain (IR) of at least 15%. IR is calculated as $(x-y/x) \times 100$ where x is the ionicity measured after applying standard shear and y is the ionicity of the polymer before applying standard shear.

These values are best determined by forming a 1% composition of the CP in deionised water, allowing this to age for 2 hours and then further diluting it to 0.1% active CP. The ionicity of the CP, y , is measure by Colloid Titration as described by Koch-Light

5 Laboratories Limited in their publication 4/77 KLCD-1.
(Alternatively the method described in GB-A-1,579,007 could possible by used to determine y). The ionicity after shear, x , is determined by measuring by the same technique the ionicity of this solution after subjecting it to standard shear.

10 The shear is best applied to 200ml of the solution in a substantially cylindrical pot having a diameter of about 8cm and provided in its base with a rotatable blade about 6cm in diameter, one arm of the blade pointing upwards by about 45 degrees and the other downwards by about 45 degrees. The blade is about 1mm thick
15 and is rotated at 16,500 rpm in the base of the pot for 10 minutes. These conditions are best provided by the use of a Moulinex homogeniser but other satisfactory conditions can be provided using kitchen blenders such as Kenwood, Hamilton Beach, Iona or Osterizer blenders of a Waring Blender.

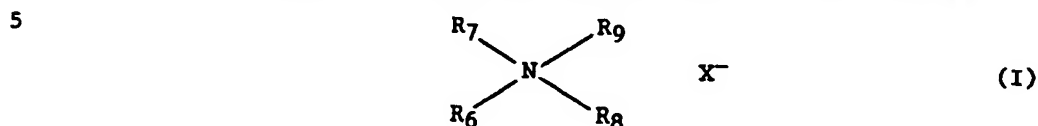
20 In practice the precise conditions of shear are relatively unimportant since, provided the degree of shear is of the same order of magnitude as specified, it will be found that IR is not greatly affected by quite large changes in the amount, for instance the duration of shear, whereas at lower amounts of shear (for instance 1
25 minute at 16,500 rpm) IR is greatly affected by small changes in shear. Conveniently therefore the value of x is determined at the time when, with a high speed blade, further shear provides little or no further change in ionicity. This generally requires shearing for 10 minutes, but sometimes longer periods, e.g., up to 30 minutes
30 with cooling, may be desired.

The CP's used in the invention preferably have IR above 30%, often in the range 35 to 45%. IR may increase from zero at zero cross linker up to a peak or plateáu at a level around, for instance 10 to 25 ppm, cross linker and preferably IR is at or near this peak
35 or plateáu, generally at as low a level of cross linking as is

consistent with the high IR value.

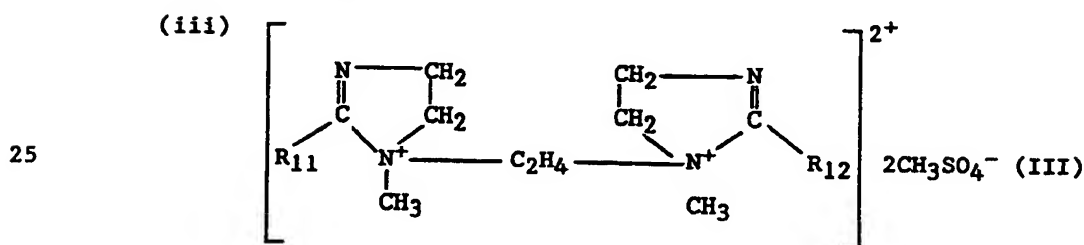
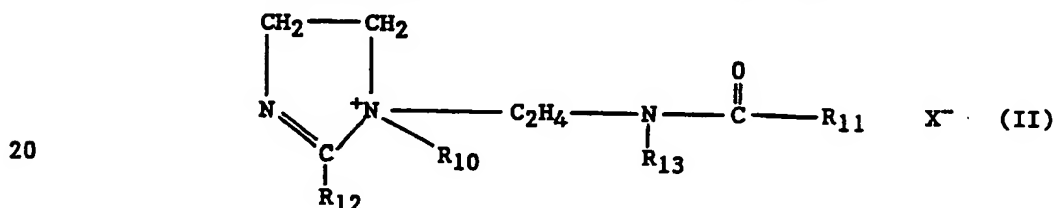
The water dispersible cationic softener used in the fabric conditioning formulation may be selected from:

(i) dihydrocarbyldialkylammonium salt of the formula:

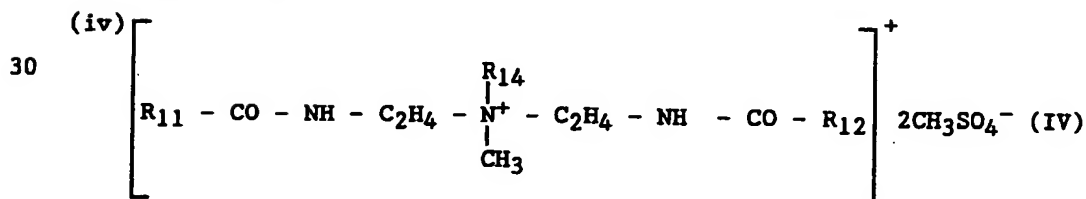


wherein R_6 and R_7 are the same or different C_8 to C_{24} alkyl or alkenyl groups, which may optionally carry additional functional groups selected from $-\text{OH}$, $-\text{O}-$, $-\text{CONH}-$ and $-\text{COO}-$ either as substituents or as part of the main alkyl or alkenyl chain, R_8 and R_9 are the same or different C_1 - C_4 alkyl, hydroxyalkyl or (poly)oxyalkylene groups, and X^- is an anion selected from a halide, methosulphate and ethosulphate,

(ii) an alkylimidazolinium salt of the formula (II):



and



where in (ii), (iii) and (iv) above R_{10} is a C_1 - C_4 alkyl or hydroxyalkyl or (poly)oxyalkylene group, R_{11} and R_{12} are the same or

different alkyl or alkenyl groups containing from 8 to 24 carbon atoms, R_{13} is hydrogen, a C_1 - C_4 alkyl or a $-CO-R_{11}$ group and X^- is an anion, selected from a halide, methosulphate or ethosulphate, and $R_{14} = H$, alkyl, hydroxyalkyl or (poly)oxyalkylene.

5 Examples of these cationic softeners of formula (I) above include: dieicosyldimethyl ammonium chloride; didocosyldimethyl ammonium chloride; dioctadecyldimethyl ammonium chloride; dioctadecyldimethyl ammonium methosulphate; ditetradecyldimethyl ammonium chloride and naturally occurring mixtures of above fatty
10 groups, e.g. di(hydrogenated tallow) dimethyl ammonium chloride; di(hydrogenated tallow) dimethyl ammonium methosulphate; ditallow dimethyl ammonium chloride; and dioleyldimethyl ammonium chloride. Di(hydrogenated tallow) dimethyl ammonium chloride or dioctadecyl dimethyl ammonium chloride is preferred.

15 In the cationic softener represented by formula (I), each of R_6 and R_7 suitably represents a substituent in which more than 50%, preferably more than 75%, of the groups are C_{12} to C_{18} alkyl or alkenyl groups. More preferably, each of the substituent groups R_6 and R_7 represent a mixture of alkyl and alkenyl groups, namely from
20 50-90% C_{18} alkyl or alkenyl groups and from 10 to 50% C_{16} alkyl or alkenyl groups.

Thus, the substituents R_6 and R_7 are most preferably represented by dioctadecyl groupings, the substituents R_8 and R_9 are preferably methyl groups, and the anion X^- is preferably a chloride.

25 Thus, the preferred softener of formula (I) is di(hydrogenated tallow) dimethyl ammonium chloride or dioctadecyl dimethyl ammonium chloride.

Examples of the imidazolinium salts of formula (II) above include
30 1-methyl-1-(tallowylamido-) ethyl -2-tallowyl-4,5-dihydroimidazolinium methosulphate and 1-methyl-1-(palmitoylamido)ethyl -2-octadecyl-4,5-dihydro-imidazolinium methosulphate. Other useful imidazolinium materials are
35 2-heptadecyl-1-methyl-1(2-stearoylamido)-ethyl-imidazolinium methosulphate and 2-lauryl-1-hydroxyethyl-1-oleyl-imidazolinium

chloride. Such imidazolinium fabric softening components are described more fully in US Patent No. 4127489 and can be used in the formulations of the present invention.

5 The water-dispersible cationic softeners referred to herein are commercially available materials under the following trade names or Registered Trade Marks: Dehyquart DAM (ex Henkel et Cie); Arquad 2HT (ex AKZO); Prapagen WK (ex Hoechst); Noranium M2SH (ex CEKA); and the imidazolinium compounds falling within (a) are Rewoquat W7500H, Rewoquat W7500 and Rewoquat W3690 (all ex REWO), Casaquat 865 & 888
10 (ex Thomas Swan) and Blandofen CAZ-75 (ex GAF).

The pH of the formulation is maintained at a value from 2.5 - 5, preferably from 3.0 - 4.0 in order to achieve optimum performance.

15 The CP thickener is suitably used as a 50%w/w dispersion in a mineral oil.

The CP thickener of the present invention is opaque when dispersed in water. Depending upon the concentrations used, if the thickener is used in sufficient quantities, no additional opacifier will be needed. However, at relatively low concentrations of the
20 thickener, a supplementary opacifier may be incorporated.

The formulations of the present invention may contain in addition one of the following as non-ionic softener extenders and/or stability improvers and/or rheology modifiers: such as ethoxylated amide, alcohols, acids and esters with not more than 7EO groups;
25 fatty acid ester or preferably partial ester of mono or polyhydric alcohol or anhydride thereof having from 1-8 C atoms; esters of fatty alcohols having from 12-24 C atoms and mono or polycarboxylic acids with 1-8C atoms; and R3XR4 where: R3=12-24C R4=1-6C neither interrupted by more than one oxygen link; X= Sulphur, NHCO or CONH.

30 The aqueous fabric softening formulations can be made by direct addition of the thickener to the aqueous based softener containing the non-ionic and cationic softeners.

It is preferably made by the addition of the cationic and non-ionic softeners in water containing other minor ingredients to
35 an aqueous dispersion of the CP thickener, or, most preferably by

dispersing the CP thickener in a molten pre-mix made up of the cationic softener alone or combined with the other coactives and then dispersing the pre-mix into the aqueous seat which may also contain other minor ingredients.

5 Alternatively, the thickener may be initially diluted gradually to a paste like consistency and then brought to the final concentration.

10 A feature of the invention is that the cationic softeners in the formulation appear to enhance the thickening ability of the thickeners by an order magnitude when compared with the performance of such thickeners in the absence of cationic components.

The present invention is further illustrated with reference to the following Examples.

Examples

15 For the sake of simplicity, the following experiments were carried out with a softening formulation which was an aqueous solution containing a cationic softener to which was added the thickener of the present invention and the improvement in viscosity and opacity monitored.

20 A reverse phase dispersion was formed by dispersing into a conventional reverse phase non-aqueous liquid containing emulsifying agent and amphipathic stabiliser an aqueous monomer blend consisting of 80% by weight dimethylaminoethyl methacrylate methyl chloride quaternary salt and 20% acrylamide and 15ppm methylene bis
25 acrylamide. The mixture was degassed and initiated in the conventional manner and polymerisation was allowed to go to completion. The mixture was then subjected to azeotropic distillation to provide a substantially anhydrous dispersion of polymer particles less than 2 micrometers in size dispersed in
30 mineral oil (50%w/w) which was Shell oil 60 Solvent Pale. This CP is designated polymer R below.

35 The solutions were prepared by initially dispersing the thickener in a cationic softener and then mixing this dispersion with water using a high temperature (65°C) and vigorous mixing (200 - 300 rpm) to produce a formulation.

It was found that in the absence of the polymer R thickener, a cationic softener, distearyl dimethyl ammonium chloride (DSDMAC) gave a thin product (viscosity ca. 20cP at 20 Sec⁻¹ at 25°C) when used in concentrations of 3%w/w and at a pH in the range of 3 - 3.9. However, in the presence of 0.2%w/w of the 50% w/w dispersion of CP in oil and using only 2.0%w/w of DSDMAC, a good viscous product (viscosity 250-260 cP at 20Sec⁻¹ at 25°C) was obtained at the same pH range.

The performance of the thickeners of the present invention is shown in the Tables below. In the Tables, the reference to viscosities is based on measurements carried out at 20 sec⁻¹ at 25°C using a Haake viscometer. The shear rates specified correspond to that of liquids when being poured or when running down surfaces.

Table 1

Illustrates the thickening power of the polymer R thickener used in the present invention as represented by a plot of aqueous viscosity η that of two of the most effective polymer thickeners conventionally used, i.e. NATROSOL HHBR (Registered Trade Mark) which is a cellulose ether, and a cationic guar gum (Jaguar C-13-S).

Table 2

Illustrates (a) the synergistic thickening effect of a cationic softener active (DSDMAC) when combined with the polymer R thickener of the present invention and (b) the near linear relationship between polymer level and viscosity.

Table 3

Illustrates the synergy of the cationic softener (a distearyl imidazolinium methosulphate) with the polymer R thickener of the the present invention when compared with the thickener alone. This Table 3 also includes the performance of the guar gum and the cellulose ether for comparison.

A potentially unique combination property is that, unlike soluble thickening polymers, the CP thickeners of the present invention are opaque when dispersed in water. The opacifying power of the CP thickeners of the present invention when compared with a

conventional styrene-acrylamide opacifier used in fabric conditioners was found to be indistinguishable at 0.2% over the visible spectrum and, in fact, better than the conventional thickener at ca. 0.1%w/w concentration. For application in fabric conditioners, the CP thickeners of the present invention do not affect rewettability, nor do they build up on cloth in multi-cycle washing. It was found not to interfere with softening.

It has a considerable advantage in thickening fabric conditioners as they do not precipitate cationic actives between pH 3-4.

Where the CP thickeners of the present invention are precipitated, unlike other polymers, they are easily redispersed as they tend not to flocculate the cationic softener.

Physical stability of the CP thickeners of the present invention are easily quantified. At pH values from 3 to 5 the CP thickener is indefinitely stable over all storage regimes e.g. in the DSDMAC and imidazolinium cationic softener dispersions.

Other advantages of the CP thickeners of the present invention are that (a) as a synthetic thickener, the thickening is less likely to be lost as a result of the action of bacterial or enzymic activity, (b) at low levels of use, there is no "stringy" rheology, but at low shear rates e.g. at 5 sec^{-1} and 0.2%w/w concentration (of 50%w/w dispersion in oil) it exhibits a dynamic viscosity of about 28cP in contrast to conventional NATROSOL HHBR which has a dynamic viscosity of 30cP under the same conditions, and (c) where the viscosity of the finished product is attributable to the thickener alone, the substantially linear relationship between the concentrations used normally in such formulations and the viscosity obtained means that there are no sudden fluctuations of viscosity by marginal variations in dosage of the CP thickener unlike conventional polymers where this relationship can be exponential.

Table 1VISCOSITY IN WATER

	<u>% THICKENER</u>	<u>POLYMER R*</u>	<u>NATROSOL HHBR</u>	<u>JAGUAR C-13-S</u>
	0.1	56	5	10
5	0.2	110	10	20
	0.3	170	50	60
	0.4	230	155	160

Table 2VISCOSITY OF POLYMER R IN DSDMAC

	<u>% POLYMER R*</u>	<u>2% DSDMAC</u>	<u>3% DSDMAC</u>
10	0.0	20	21
	0.05	65	75
	0.1	130	150
	0.15	195	225
15	0.2	260	300

Table 3VISCOSITY IN 3% REWOQUAT 7500**

	<u>% THICKENER</u>	<u>POLYMER R*</u>	<u>NATROSOL HHBR</u>	<u>JAGUAR C-13-S</u>
	0.0	8	8	8
20	0.05	50	15	20
	0.1	100	25	45
	0.15	150	50	60
	0.2	200	70	90

ALL VISCOSITIES MEASURED AT 20 SEC-1 AT 25 DEGREES CELSIUS ON HAAKE
 25 ROTOVISCOMETER USING M5 MEASURING SYSTEM AND MV1 BOB AND CUP

* Quantities used are based on a 50% w/w dispersion of polymer R in mineral oil.

** distearyl imidazolinium metho sulphate, Regd. Trade Mark, ex REWO.

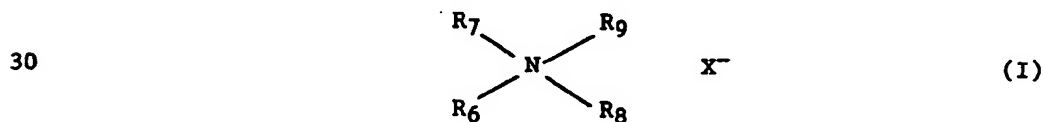
Claims

1. As aqueous based fabric conditioning formulation comprising a water-dispersible cationic softener and a thickener characterised in that the thickener is a cross-linked cationic polymer that is derivable from a water-soluble cationic ethylenically unsaturated monomer or blend of monomers which is cross-linked by 5 to 45ppm of a cross-linking agent comprising polyethylenic functions.
2. A formulation according to Claim 1 wherein the cross-linked cationic polymer is derivable from monomers comprising acrylic monomers.
3. A formulation according to Claim 1 or 2 wherein the cross-linked cationic polymer is derivable from monomers comprising one or more of
 - (a) dialkylaminoalkyl-acrylates or -methacrylates,
 - (b) dialkylaminoalkyl-acrylamides or -methacrylamides, or
 - (c) the quaternary or acid salts of either (a) or (b).
4. A formulation according to any one of the preceding Claims wherein the cross-linked cationic polymer is derivable from a mixture of cationic monomers and nonionic monomers.
5. A formulation according to Claim 4 wherein the nonionic monomer is selected from acrylamide, methacrylamide, N-vinyl pyrrolidone, and lower alkyl water insoluble (meth)acrylic monomers.
6. A formulation according to any one of the preceding Claims wherein the cross-linked cationic polymer has a particle size below 10 micrometers.
7. A formulation according to Claim 7 wherein the particles are formed by polymerising the ethylenically unsaturated monomer in the

presence of a cross-linking agent.

8. A formulation according to any one of the preceding Claims wherein the cross-linking agent is selected from methylene bis acrylamide, ethylene glycol di-acrylate or -methacrylate, diacrylamide, cyanomethylacrylate, vinyloxyethyl-acrylate or -methacrylate, formaldehyde, glyoxal and a metal salt.
9. A formulation according to any one of the preceding Claims wherein the cross-linked cationic polymer is formed from a blend of 0-40%w/w of acrylamide and 100-60%w/w of a quaternary ammonium salt of dialkylaminoethyl methacrylate cross linked with 10 to 40 ppm of a cross linking agent.
10. A formulation according to any one of the preceding Claims wherein the cross-linked cationic polymer is present in an amount from 0.01-0.5%w/w based on the total aqueous fabric conditioning formulation.
11. A formulation according to any one of the preceding Claims wherein the cross-linked cationic polymer has a notional molecular weight of 5,000,000 to 30,000,000 and an intrinsic viscosity above 4 dl/g prior to cross-linking.
12. A formulation according to any one of the preceding Claims wherein the cross-linked cationic polymer is cross-linked with at least 5% w/w of dialkylamino alkyl acrylate and has a degree of non-linearity such that the cationic polymer has an ionic regain of at least 15%.
13. A formulation according to any one of the preceding Claims wherein the formulation contains a water-dispersible cationic softener selected from

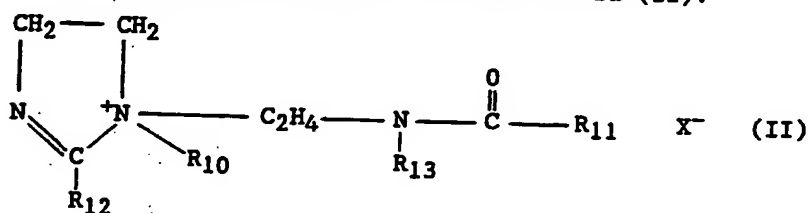
(a) a dihydrocarbyldialkylammonium salt of the formula:



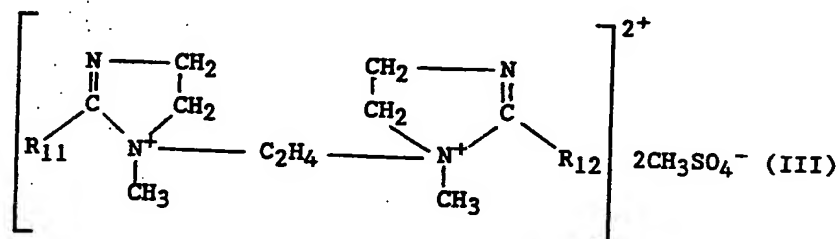
wherein R_6 and R_7 are the same or different C_8 to C_{24} alkyl or alkenyl groups, which may optionally carry additional functional groups selected from -OH, -O-, -CONH- and -COO- either as substituents or as part of the

main alkyl or alkenyl chain, R_8 and R_9 are the same or different C_1 - C_4 alkyl, hydroxyalkyl or (poly)oxyalkylene groups, and X^- is an anion selected from a halide, methosulphate and ethosulphate,

(ii) an alkylimidazolium salt of the formula (II):

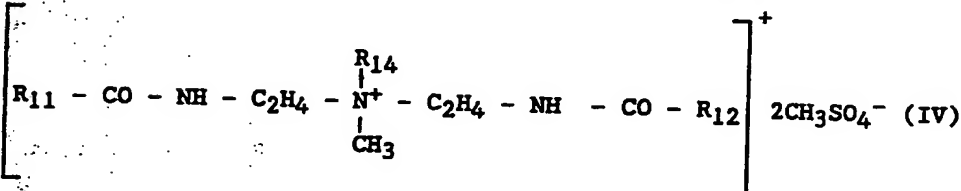


(iii)



and

(iv)



where in (ii), (iii) and (iv) above R_{10} is a C_1 - C_4 alkyl or hydroxyalkyl or (poly)oxyalkylene group, R_{11} and R_{12} are the same or different alkyl or alkenyl groups containing from 8 to 24 carbon atoms, R_{13} is hydrogen, a C_1 - C_4 alkyl or a $\text{CO}-R_{11}$ group and X^- is an anion, selected from a halide, methosulphate or ethosulphate, and $R_{14} = \text{H}$, alkyl, hydroxyalkyl or (poly)oxyalkylene.

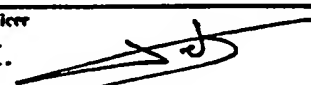
14. A formulation according to any one of the preceding Claims wherein the pH of the formulation is from 2.5-5.0.

15. A formulation according to any one of the preceding Claims wherein the cross-linked cationic polymer is used in the formulation as a 50%w/w emulsion in mineral oil.

INTERNATIONAL SEARCH REPORT

PCT/GB 90/00600

International Application No.

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC ⁷		
Int.Cl. 5 C11D3/37 ; C11D1/62		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C11D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0299787 (KAO CORPORATION) 18 January 1989 see pages 2 - 4, line 10 see page 4, line 45 - page 6, line 16 see pages 10 - 11	1-5, 13
A	---	6-12, 14
A	GB,A,2204608 (KAO CORPORATION) 16 November 1988 see the whole document	1, 13
A	---	1, 13
A	EP,A,0043622 (THE PROCTER & GAMBLE COMPANY) 13 January 1982 see page 11, line 32 - page 14, line 7; claims 1-3, 5	1, 13
A	---	2-9
A	US,A,4737541 (D.L. STAVENGER) 12 April 1988 see the whole document	2-9
<p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
19 JULY 1990	10 AOUT 1990	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	TETAZ F.C.E. 	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 90/00600

SA 36219

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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19/07/90

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US-A-4737541	12-04-88	None	